

Rocky Flats Environmental Technology Site

Actinide Migration Studies

Meetings January 21-22, 1999

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Summary and recommendations for path forward

Particulate transport continues to be the dominant transport pathway identified for the Pu and Am actinides off the Site, based on surface water characterization, soil redox reaction process experiments and erosion modeling. The recent papers in Nature on colloid transport at the Nevada Test Site were discussed extensively. We continued discussion of end-state planning and concepts. The impact and detailed operations of grasslands, wetlands and settling ponds is not clear, given the present understanding of contaminant distribution and transport via surface water. Completion of 903 Pad characterization, new aseptic groundwater wells and ongoing actinide migration studies (colloid distributions, soil particulate and redox reaction characterization, air transport modeling) are important components of improvements in our understanding, and will require integration into remediation planning.

Solar Pond remediation basis and planning was presented. Recently completed uranium isotopic analysis results were presented for selected solar ponds plume and background samples. This work has significantly enhanced characterization of this contamination problem, and replaced simplified assumptions with quantitative data. Coupled with these improvements in characterization, the geochemical modeling effort needs to define tests for our geochemical and transport understanding.

Progress and integration

Characterization of erosion, air transport, contaminant distributions, chemical/physical contaminant signatures (U isotopics, Pu and Am concentrations and ratios) and redox processes continue to be advanced. Further integration between site characterization and remedial actions inside and outside the Protected Area will be essential. Air modeling efforts require integration. Integration and application of results to further detailed development of the conceptual model should continue to be a focus of AMS discussions during the year to maximize value and applications to the site.

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Results presented

Win Chromec – Erosion Modeling update

The discussion on this program indicates a reasonable approach is being followed in modifying the models to improve their value as predictive tools on how to reduce migration, including solar pond flow, vegetation and air erosion. Next year the plan is to use the models for various future scenarios. However, prior to that, there is a need to confirm the predictions of the models by comparison with data obtained from sampling. This should be given careful consideration. Also, it is worth noting that there is much talk at present about reducing the erosion of bare slopes by growing grass. However, this does not take into account that periodic dry spells over the next thousands of years, which would reduce the retention by grass and, therefore, potentially allow increased migration.

Lane Butler & Steve Paris – 903 Pad remediation basis

The status of 903 Pad area site characterization in preparation for definition of remedial actions was presented. This effort has involved measurements of actinides and VOCs from 903 Pad borehole samples and a broader surface HPGE and soil sample assay survey, with the goal of estimating the volume of soils that will require remediation in and around 903 pad. The actinide data set, in particular for Am and Pu, should be used to evaluate transport, source and potential for reactive transformations. Given the large volumes of soil involved, institutional and/or management controls were raised as possible remedial action components for at least some of the area. Previous capping and water management actions provide a baseline for evaluation, and must be integrated with planning for overall site water management (e.g. transition from active pond management to flow through wetlands).

Lane Butler & Annette Primrose – Solar Pond remediation basis

Mike Murrell and Chris Birk – Uranium Isotopic analyses

Annette Primrose presented an update on the SPP remediation plans. The nature of the uranium plume and the treatment alternatives for the nitrate plume have received a considerable amount of attention. Nitrate must meet in-stream water quality standards of 100 mg/L (until 12/09) and uranium must meet 10 pCi/L.

Determinations of $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ activity ratios were obtained on 16 ground water samples collected from wells in the SPP area. The analyses were done at Los Alamos National Laboratory (LANL) by High Resolution-Inductively Coupled-Mass Spectrometry (HR-ICP-MS) and Mike Murrell and Chris Brink, both of LANL, explained the technique and the significance of the data. Since natural uranium has a constant $^{235}\text{U}/^{238}\text{U}$ ratio of 0.72% and no detectable ^{236}U , a plot of one activity ratio against the other can distinguish those waters that contain natural uranium from those containing anthropogenic uranium. Of the sixteen wells sampled, five showed anthropogenic signatures and the other eleven appeared to be natural. Of the eleven samples, however, seven are not shown on SPP maps and come from areas outside the industrial and contaminant areas. Three of the eleven samples come from the Walnut Creek drainage immediately down drainage from the SPP and not from the SPP itself. That leaves one site indicated as having natural uranium from the SPP and that one sample (well P209889) has a $^{236}\text{U}/^{238}\text{U}$ ratio that may be within detection and should be rechecked to see if it is a mixture of natural and anthropogenic uranium and possibly monitored. These results suggest that a large portion of the uranium plume may be natural but the data is extremely meager. Other naturally high uranium concentrations have been noted in ground waters at RFETS away from the industrial and contaminated areas. Two important issues were brought up with regard to this characterization. The first is in regard to the adequacy of the well coverage that defines both the natural and anthropogenic uranium plumes and the second is the estimate of errors for the isotope activity ratios.

Although it has been suggested that a large portion of the uranium plume coming from the Solar Ponds area is natural, the sampling and the well distribution for sampling are not adequate to define how much is natural vs. anthropogenic. The wells sampled include five that are clearly anthropogenic and this coverage is very spotty considering the size of the area. The sampling is not adequate to indicate whether the anthropogenic plume is migrating only northeast toward Walnut Creek or if part of it is migrating southeast. It is not adequate to tell us if a

significant plume of anthropogenic uranium is migrating from building 774 and others nearby where major spills are known to have occurred. Large areas where the plume is expected to be have no wells. Two to four nested wells should be installed to correct this obvious gap in well distribution. The sampling is not adequate to determine whether the uranium plume is largely natural or largely anthropogenic because there is only one well on the SPP area that appears to be natural from one sampling event and one analysis and even that well has a hint of the anthropogenic signature. It is possible that the uranium plume as mapped previously, based solely on uranium concentrations, could be mostly anthropogenic.

With regard to the error estimates on the uranium isotope data, it was noted that when the $^{236}\text{U}/^{238}\text{U}$ activity ratio was at or below detection the numbers were often reported as a negative number and this is not possible. The cause of this was the low concentrations and uncorrected background adjustments that made background higher than the sample values. The suggestion was made to properly evaluate the errors near the detection limits and to apply statistics to determine the detection limits for the ^{236}U concentrations.

After exploring various alternatives for remediation of the SPP, the current plan is to evaluate the use of a new, deep interception trench along the road that would collect the contaminant plume and transport it to a nearby container with reactive material to reduce the nitrate and uranium with organic matter.

Plans presented and discussed

Martha Hyder – Air Modeling

A task plan for air modeling efforts during this fiscal year was presented. While the task plan encompasses the general areas of work to characterize and model atmospheric transport of actinides at Rocky Flats, integration and evaluation is weak. In particular, integration with existing monitoring programs at the site is essential in the evaluation of sensitivity analyses of emission, deposition and dose. Previous modeling efforts focused on Rocky Flats and actinide transport provide a substantial basis for evaluating models and defining key problem and integration areas. In addition, other DOE sites such as Hanford and Nevada Test Site should be used to provide parallel information and modeling results.

Jeb Love – Pu fate/transport and daily loading

Based on an integrated evaluation of CDPHE, RFETS and AMS monitoring and characterization of processes, an assessment of the status of the conceptual model for migration of actinides was presented. Included in this assessment was a valuable breakdown of margins of safety included in the regulatory limits presently being utilized. Four key areas that AMS should continue to emphasize and utilize can be extracted from this presentation: (1) continued integration and quantification of conceptual model by AMS and the site, (2) potential value and validity of total maximum daily load basis for evaluating actinide migration, (3) continued demonstration and evaluation of best management practices (BMPs) for short- and long-term erosion control of soil areas, and (4) the importance of evaluating real data on performance of pond and proposed wetland systems for actinide migration control in surface waters. In addition, our discussions raised important questions about the present basis for understanding actinide interactions with organic materials and migration processes across the diversity of grasslands, ponds and wetlands present at Rocky Flats.

Kathleen Meyer (RAC) – RSALs support

We received an informational briefing on the ongoing work by RAC on soil action levels. Issues that they will be working on include review of soil action levels at other sites, evaluation of strengths and weaknesses of risk assessment codes, and plutonium solubility in soil and surface water. The focus is on onsite soil action levels that will protect all eventual users. We agreed that continued discussions would be valuable and look forward to being kept informed of the results of this work.

Discussion of FY99 efforts

Redox experiments and next steps

We discussed experimental redox potentials during the AMS meetings and agreed that +300 mV would not only fill in an obvious gap in the present data sets, but it also is in that range of moderately reducing conditions that might be expected for the soils at RFETS, especially flooded soils with some organic matter present. These conditions could be described as "suboxic" - i.e. where dissolved oxygen is absent and manganese and iron could be reduced but not sulfate.

The other important study with the redox cell would be to add an iron oxide phase (hematite or goethite would make good candidates) or a manganese oxide phase (pyrolusite or possibly manganite would be good candidates) and check the reductive dissolution of these phases to demonstrate that heterogeneous reductive dissolution reactions do, in fact, take place. Grain size could affect the rate of these reactions so the solid phase should be of sufficiently small particle size to not inhibit dissolution.

Protected Area Buildings and Infrastructure - Laurie Gregory-Frost

As a follow-up to the tour of the Protected Area at the end of the October 1998 Actinide Migration Studies meeting, we discussed buildings, infrastructure and contaminant releases which need to be integrated into our understanding of the site. These discussions focused on orientation about building uses, infrastructure of pipelines, and the processes/events associated with the 1969 fire in buildings 776-777. As D&D and remediation activities develop within the Protected Area, we expect to continue these briefings and discussions in more detail so that actinide migration potential can be integrated and evaluated.

Review of documents

Review of Final Report by Bruce Honeyman

The development and application of an electrochemical cell, inert atmosphere glovebox system, and redox indicators for the monitoring and control of Eh during Pu/Am solubility studies is a very important contribution to our understanding of the behavior of Pu/Am at RFETS. This work addresses, for the first time, the longstanding hypothesis that reducing conditions (suggested to be present during the May 1995 rain event) will mobilize Pu from soils at RFETS. The reversibility of the redox indicator is a relatively good measure (QA/QC) of the integrity of the Eh measurement and maintenance system used during the experimental run. These studies appear to indicate that "operational solubility" of plutonium decreases, while the "operational solubility" of americium remains essentially unchanged under strongly reducing conditions (Eh = -90 mV). If this observation is substantiated through additional studies during FY99, then this will turn out to be a very important experimental finding. The original premise put forth by Dr. Litaor was that reducing conditions would enhance the solubility of Pu. Indeed, depending on the identity of the original "soluble" oxidation state of plutonium in the soils, this was a credible hypothesis. However, the present data do not support that hypothesis. Obviously, additional data points are needed to support or refute these new findings. At least one additional data point should be gathered between +160 and +800 mV to confirm the relative constancy of plutonium concentration in this Eh range. In addition, several new data points between +160 and -90 mV are desirable to lend additional credibility and support to the observation of decreased plutonium "operational solubility" under strongly reducing conditions.

An initial concern focused on sorption of Pu to the electrode surface, which might account for the reduced solubility at low Eh values. The investigators did make an effort to investigate this possibility. The fact that the Pu/Am ratios remain essentially constant for large and small electrodes is encouraging. Is there a significant difference in the surface area of the two electrodes?

The conclusion (number 3, page 20) that the "soluble" Pu fraction is a form of Pu(V) is not defensible based on the data available. There is no explicit oxidation state determination to support this claim. It is true that the decrease in solubility is "consistent" with a reduction of Pu(V) to Pu(IV), and that may indeed be the case, but this claim is by no means definitive. Therefore, a more cautious choice of wording should be used to denote that the data are "consistent with" the

presence of Pu(V) in the solution and solid phases. Other potential changes in the substrate that could result in fixation of plutonium should be considered and discussed in future documents.

The approximate level of agreement between the selective extraction experiments reported here, and those reported previously by Litaor and Ibrahim, is encouraging. While the order of application of extractants can give rise to experimental differences, slight variations in procedure (chemicals, mixing times, etc.) from laboratory to laboratory can also lead to slight differences in the outcome. However, both sets of data do indicate similar trends that (i) the exchangeable fraction is tiny, and (ii) the operationally defined "organic" and "residual" fractions are high. Last year's CSM data agree well with the present work, and we complement professor Honeyman's staff for their careful work.

Review of Final Report on Phase Speciation.....by P. Santchi.

The initial filter passing experiments have demonstrated that there is very little (operationally defined) "dissolved" plutonium in the solutions taken from GS03 on Walnut Creek. Plutonium concentrations are in the femtomolar range, and are typical of global fallout. The data also indicate that the bulk of plutonium and americium (80 - 90%) was associated with particles and colloids. This work is important for the Site in that it indicates that "dissolved" plutonium is of minor importance as a transport pathway and/or reaction mechanism for migration of plutonium in ground and surface waters at RFETS. These data also indicate that future efforts should continue to focus on particulate and colloid-facilitated transport pathways.

We have some comments on the QA/QC documentation. It appears that standard calibration procedures were followed. There are statements about the use of Pu(IV) and Pu(VI) yield tracers both on page 1, 6, and appendix III. Statements about NIST traceability of plutonium isotopes are given, but there is no discussion about how Pu(IV) or Pu(VI) were prepared, or the oxidation states verified. If the oxidation state is important to the experiment, then documentation should be provided about the manipulation of plutonium solutions to generate Pu(IV) and Pu(VI) and what measurements were performed to assure that these indeed were the oxidation states employed.

Form of Pu in environment, Colloid mobility and Nature paper

The Nature Article and the Implications for Rocky Flats Actinide Migration Studies

The article in *Nature* on the observation that Pu has been observed from weapons shots as much as 13 km distance from the site of the shot is interesting. This is a surprisingly far distance and the mechanism of transport is still not ascertained. However, of relevance to Rocky Flats is the fact that the authors propose the migration by a colloidal nature for the Pu. This is not surprising, and is generally accepted by scientists around the world that the migration of Pu in natural systems is, indeed, due to colloids. If the concentration of Pu is sufficiently large, there may be intrinsic colloids - that is, colloids formed of plutonium directly - as the polymeric $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. In fact, this is the form present in the colloids from test shots, as such material would be produced as a result of a nuclear explosion. However, in the plutonium at Rocky Flats which would be released from processing systems, etc., the plutonium is more reactive and also at a much lower concentration. Consequently, it is unlikely to form intrinsic colloids, but, rather, would be sorbed onto the surfaces of other colloids such as clay or humic materials. These colloids, in turn, would transport the plutonium in the form of "pseudo-colloids". In summary, except for the extent of the plutonium migration in the *Nature* report, there is little that wasn't known in terms of the nature of the mode of transport, etc. However, it is very important in relating any of these systems to Rocky Flats, to keep in mind that the basic nature of the plutonium present is different, since the plutonium discussed in the article comes from high fired materials produced in a weapons explosion compared to the Rocky Flats plutonium from processing releases.

Most Probable Chemical Forms of Pu in RFETS Groundwaters

G. R. Choppin, D. L. Clark

The probability of release of plutonium from RFETS soils to the surrounding environment will be determined by a variety of factors, some of which are currently being addressed by Actinide Migration Studies. The fate and transport of plutonium will be governed by the solubility

of its compounds in groundwater and surface waters, the tendency of plutonium compounds to be adsorbed onto mineral phases in soil particles, and by the probability that the colloidal forms of plutonium will be filtered out by the soil or rock matrices, or adsorb or settle out during transport

The solubilities of plutonium compounds will depend largely on the oxidation state. Plutonium is unique in that it can exist in four different oxidation states in natural water/rock systems. As in the case of other polyvalent metal cations, the lower oxidation states of plutonium are more stable in acid solution, and the higher oxidation states are more stable in basic solution. Complexation can alter these generalizations. The greater complexing strength of Pu(IV) causes Pu(III) to be oxidized to Pu(IV) in neutral media.

Generally, plutonium will exist in aqueous solution as Pu(V) and Pu(VI) with Pu(V) predominating in oxidized natural waters. For plutonium in the lower oxidation states (III) and (IV), the solubilities are generally exceedingly low. Oxidation or reduction of higher oxidation states can lead to the formation of colloidal forms of "Pu(OH)₄" or "PuO₂ · 2H₂O" often referred to as "plutonium hydrous oxide" or "Pu(IV) polymer". Pu(IV) colloids are often kinetically very stable in solution, but eventually tend to be absorbed or filtered out due to interactions with mineral and soil phases. The slow crystallization of Pu(IV) colloids leads to greater stability and lower solubility.

In natural waters plutonium solubility is limited by the formation of amorphous Pu(OH)₄ or polycrystalline PuO₂. A reasonable estimate for the solubility product (K_{sp}) of Pu(OH)₄ is approximately 10⁻⁵⁴. This estimate puts an upper limit on the amount of Pu that can be present, even if Pu(V) or Pu(VI) are the more stable solution forms. Pu(V) has a low tendency to hydrolyze and form complexes with ligands, and is much less likely to be sorbed to solid surfaces and colloidal particles than the other oxidation states of plutonium. As a result, plutonium can be expected to migrate most rapidly if it is in the pentavalent oxidation state. The total solubility, however, is still limited by the formation of the highly insoluble amorphous Pu(OH)₄. Sorption of hydrolyzed Pu(IV) in natural water on mineral surfaces and surfaces coated with organic material is accountable for the very low concentrations of dissolved Pu even in the absence of Pu(OH)₄ (am) or PuO₂ (c). The strong tendency of Pu(OH)₄ to sorb on surfaces is a dominant and often controlling feature in plutonium geochemistry.

In addition, the insoluble Pu(OH)₄ is known to undergo an "aging effect" that reduces its solubility even further. Following the initial precipitation of Pu(OH)₄, this species rather quickly (weeks-months) begins a partial dehydration process to form a polymeric oxo-bridged plutonium system that significantly decreases the solubility. For example, recently precipitated Pu(OH)₄ can be readily dissolved by making the aqueous solution strongly acidic. However, as the precipitate ages over a period of months, a decreasing fraction of the precipitated plutonium re-dissolves by this acid treatment. Precipitates that have aged for several years usually show very little solubility with strong acid treatment and require oxidation to the hexavalent state for re-dissolution. Therefore, it is rather commonly accepted that a major aspect of the very strong insolubility of Pu(IV) in natural systems is related to this aging effect, producing the oxo-bridged Pu polymers which resist acid attack.

The data amassed during AMS studies indicate that plutonium in RFETS waters has a very low solubility, with concentrations of "soluble" plutonium in the femtomolar range, similar to global fallout. The data also indicate that plutonium is associated with colloidal particles. Since plutonium(V) has an exceedingly low tendency for sorption and complexation, the data are "consistent with" plutonium(IV) associated with the colloidal material. The extremely small amount of "soluble" plutonium (at femtomolar concentrations) is more consistent with plutonium(V).

Documents provided to advisory group

Colorado Daily news article – Study suggests Flats plutonium could be on move (Brian Hansen) 11Jan99? 2pgs

Kersting, A B , Efurd, D W , Finnegan, D L, Rokop, D J , Smith, D K , and Thompson, J L (1999) Migration of plutonium in groundwater at the Nevada Test Site Nature 397, 56-59

Honeyman, B D (1999) News & Views Geochemistry --- Colloidal culprits in contamination Nature 397, 23-24

Update figure 2 – preliminary report on soil erosion/surface water sediment transport modeling for the actinide migration study at the rocky flats environmental technology site RF/RMRS-98-285 un

Draft solar ponds plume decision document RF/RMRS-98-286 un (Jan 5, 1999)

One page summary – WEPP Erosion Modeling Update

Plant Site Plan map – from Laurie Gregory-Frost, with buildings highlighted

Air pathway fiscal year 1999 work plan

Air transport and deposition of actinides viewgraphs package

JW Love handout – Actinide Migration and Total Maximum Daily Load Status

Documents requested for advisory group

none

Participants in AMS technical meetings

<u>Name</u>	<u>Organization</u>
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